monomeric complex at lower Rh(III) concentration. An examination of this postulation is planned.

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Registry No. I, 83633-48-1; II, 83633-51-6.

Supplementary Material Available: Listings of hydrogen atom positions, general temperature factor expressions, and observed and calculated structure factors for compounds I and II (24 pages). Ordering information is given on any current masthead page.

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Synthesis and Crystal and Molecular Structure of Bis(nitrato)[diisopropyl (*N*,*N*-diethylcarbamyl)methylenephosphonate]dioxouranium(VI)

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The title complex $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$ (1) was prepared by the addition of $UO_2(NO_3)_2\cdot 6H_2O$ to the carbamylmethylenephosphonate ligand in ethanol. The compound has been characterized by infrared, ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. A single-crystal X-ray analysis of 1 has been completed at −28 °C, and the complex crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.520$ (4) Å, $b = 10.963$ (4) Å, $c = 20.033$ (8) Å, $\beta = 103.79$ (3)°, $Z = 4$, $V = 2243.7$ Å^3, and $\rho_{calcd} = 1.99$ g cm^{-3}. The structure was solved with use of heavy-atom techniques, and blocked least-squares refinement converged with $R_F = 4.1\%$ and $R_{wF} = 3.9\%$ for 4153 independent reflections with $F \geq 4\sigma(F)$. The molecular structure of 1 consists of a linear UO_2^{2+} ion surrounded at its equator by four oxygen atoms from two bidentate nitrate ions and the phosphoryl and carbonyl oxygen atoms from a bidentate phosphonate ligand. Several important bond distances include U–O(uranyl)$_{av}$ = 1.756 (6) Å, U–O(phosphoryl) = 2.420 (4) Å, U–O(carbonyl) = 2.406 (5) Å, U–O(nitrate)$_{av}$ = 2.512 (5) Å, P–O(phosphoryl) = 1.485 (5) Å, and C–O(carbonyl) = 1.260 (8) Å.

Introduction

The potentially multifunctional carbamylmethylenephosphonate (CMP) ligands, $(RO)_2P(O)CH_2C(O)NEt_2$, are known to act as efficient extractants of lanthanide and actinide ions from acidic radioactive waste solutions.[1,2] Despite intensive study of this important separations chemistry,[1,2] the details of the extraction mechanism and the stoichiometries and structures of metal–CMP complexes have not been fully revealed. Recently, synthetic and structural studies in our laboratory have begun to provide a greater understanding of this coordination chemistry. For example, it has been observed that CMP ligands coordinate with metal ions in at least three modes. Mercury(II)[3] and cadmium(II)[4] promote loss of a methylene proton at the carbon atom bridging the phosphoryl and carbonyl groups with the subsequent formation of M_2L_2 complexes in which the metal ions bond with the methine carbon atom of one ligand and the phosphoryl and carbonyl oxygen atoms of the second ligand. Thorium(IV)[5] and La(III) through Gd(III)[6] interact with two neutral CMP ligands, forming bidentate chelates through lanthanide–phosphoryl oxygen and –carbonyl oxygen atom interactions. However, the lanthanides Tb(III) through Er(III)[6] bond only with the phosphoryl oxygen atoms of two neutral ligands. This interesting variation in coordination ability of the CMP ligands is consistent with differences in extraction efficiencies under certain conditions, and additional structural studies of relevant waste-metal–CMP complexes are of interest.

Uranium species are an important constituent in many acidic radioactive waste solutions, and Schulz and McIsaac[2,7] observed that UO_2^{2+} is extracted by CMP ligands under process conditions. Elaborating on this study, Horwitz and co-workers[8] recently suggested that dihexyl (*N*,*N*-diethylcarbamyl)methylenephosphonate (DHDECMP) acts as a neutral extractant toward UO_2^{2+}, and on the basis of distribution ratios, an extraction stoichiometry DHDECMP:UO_2^{2+} = 2 was proposed. In addition, infrared and thermodynamic data were used to suggest that the CMP ligand functions only as a monodentate ligand through uranium atom–phosphoryl oxygen atom interactions.

As part of our studies of the coordination properties of CMP ligands with transition, lanthanide, and actinide metal ion species, we have explored the chemistry of diisopropyl (*N*,*N*-diethylcarbamyl)methylenephosphonate (DiPDECMP) with UO_2^{2+} in nitric acid solution. We report here, the formation, spectroscopic characterization, and single-crystal X-ray diffraction analysis of the resulting complex $UO_2(NO_3)_2$(DiPDECMP).

Experimental Section

General Information. The DiPDECMP ligand was prepared by literature methods.[1] $UO_2(NO_3)_2\cdot 6H_2O$ was obtained from City Chemical Corp. Infrared spectra were recorded on a Nicolet Model 6000 FT IR spectrometer from KBr pellets. NMR spectra were recorded on a Varian FT-80 spectrometer operating at 32.2 MHz (^{31}P), 20.0 MHz (^{13}C), and 80.0 MHz (^1H). The samples, dissolved in an internal deuterium lock solvent, were contained in 5-mm tubes. Spectral standards were 85% H_3PO_4 (^{31}P) and Me_4Si (^{13}C and ^1H). Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN.

Preparation of the Complex. The complex was prepared by addition of 12 mmol of $UO_2(NO_3)_2\cdot 6H_2O$ to 24 mmol of DiPDECMP in ethanol. The mixture was heated, and a milky yellow solution was obtained immediately. The solution was filtered, and a light yellow solid was collected. The solid was washed with ethanol and redissolved

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Table I. Experimental Data for the X-ray Diffraction Study of $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$

(A) Crystal Parameters at −28 °C

cryst syst: monoclinic
space group: $P2_1/n$
$a = 10.520$ (4) Å
$b = 10.963$ (4) Å
$c = 20.033$ (8) Å
$\beta = 103.79$ (3)°
$Z = 4$

mol wt = 673.4
$V = 2243.7$ Å^3
$\rho_{\text{calcd}} = 1.99$ g cm^{-3}
$\rho_{\text{exptl}} = 1.98$ g cm^{-3}
$\mu = 92.1$ cm^{-1}
$F(000) = 1288$

(B) Data Collection

diffractometer: Syntex P3/F
radiation: Mo Kα ($\bar{\lambda} = 0.71069$ Å)
monochromator: highly oriented graphite cryst
reflctns measd: $\pm h, +k, +l$
2θ range: 1–57°
scan type: θ–2θ
scan speed: 5.9–29.3° min^{-1}
scan range: $[2\theta(K\alpha_1) - 1.0]°$ to $[2\theta(K\alpha_2) + 1.0]°$
bkgd measmt: stationary cryst and counter; at the beginning and end of 2θ scan, each for half the total 2θ scan time
std reflctns: 2 measd every 96 reflctns $[\bar{5}\bar{3}0, 01\bar{4}]$; no significant changes in intens obsd
unique reflctns collected: 5112
obsd reflctns used in refinement: 4153 with $F \geqslant 4\sigma(F)$
weighting scheme: $1/[\sigma(F)^2 + gF^2]$, $g = 0.00029$
no. of parameters: 278

in $CHCl_3$. Recrystallization from $CHCl_3$ resulted in a crystal suitable for X-ray diffraction analysis. The solid (**1**) was found to have the composition $UO_2(NO_3)_2[(C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$. Anal. Calcd for $UPO_{12}N_3C_{12}H_{26}$: C, 21.4; H, 3.89; O, 28.5; N, 6.24; P, 4.60; U, 35.4. Found: C, 21.5; H, 3.90; O, 28.5; N, 6.26; P, 4.42; U, 35.4. Infrared spectrum (cm^{-1}, KBr pellet): 1607 (ν_{CO}, s), 1192 (ν_{PO}, s), 1020 (ν_{POC}, s). NMR spectra ($CDCl_3$, 27 °C): $^{31}P\{^1H\}$ δ 25.5; $^{13}C\{^1H\}$ δ 171.2 ($^2J_{PC(2)} = 5.8$ Hz), 76.2 ($^2J_{PC(7)} = 7.4$ Hz), 44.8, 43.7, 30.9 ($^1J_{PC(1)} = 143.9$ Hz), 23.3, 13.7, 12.6; ^1H δ 5.09, 3.84, 3.66 ($^2J_{PH} = 19.6$ Hz), 2.13, 1.38. The crystalline solid is soluble in $CHCl_3$ and stable in air.

Crystal Structure Determination. A suitable single crystal (0.18 mm × 0.17 mm × 0.23 mm) was glued to the end of a glass fiber. The crystal was centered on a Syntex P3/F automated diffractometer, and the determinations of the crystal class, orientation matrix, and unit cell dimensions were performed in a standard manner.[5] Data were collected at −28 °C[9] in the θ–2θ scan mode with use of Mo Kα radiation, a scintillation counter, and a pulse height analyzer. A summary of the data collection parameters appears in Table I. Collected data were consistent with the monoclinic space group $P2_1/n$. Corrections for absorption were made empirically on the basis of ψ scans, and the maximum and minimum transmission factors were 0.046 and 0.019. Redundant and equivalent reflection data were averaged and converted to unscaled $|F_0|$ values after corrections for Lorentz and polarization effects.

Solution and Refinement of the Structure. Calculations were performed with the R3/SHELXTL structure determination package.[10] Anomalous dispersion terms were included for atoms with $Z > 2$. Least-squares refinement in this package uses a blocked-cascade algorithm with full-matrix blocks of 103 parameters.[11] The initial solution and refinement of the structure were based on 4302 reflections with $F \geq 3\sigma(F)$ and $\sin\theta \leq 0.48$. The uranium atom was located by Patterson methods, and the remaining non-hydrogen atoms were located by subsequent difference Fourier syntheses. Early difference maps showed residual electron density about C(10), C(11), and C(12). Disorder became apparent when the C(10), C(11), and C(12) atoms were refined with a fixed, arbitrarily small $U_{iso} = 0.05$ Å. The disorder model used was one in which the C(10), C(11), and C(12) atoms were disordered about O(3) over two sites. With $U_{iso} = 0.05$ Å, the occupancy (g_i) of the two sites was refined as ($g_{\text{minor}} = 1 - g_{\text{major}}$); g_{major} converged at 0.69. The values for the site occupancies were fixed, and the disordered group was refined isotropically. Refinement of the positional and isotropic thermal parameters gave $R_F = 7.9\%$.[12] Application of individual anisotropic thermal parameters to all non-hydrogen atoms except C(10), C(11), and C(12) gave $R_F = 4.8\%$. All hydrogen atoms were located in fixed idealized positions and their isotropic thermal parameters varied except for those on the disordered group, which were fixed at 1.2 times the U_{iso} of their parent carbon atoms. Final least-squares refinements based upon 4153 reflections with $F \geq 4\sigma(F)$ gave $R_F = 4.1\%$ and $R_{wF} = 3.9\%$. A final difference map showed the first seven peaks (1.90–0.78 e Å^{-3}) to be ≤1.03 Å from the uranium atom. The eighth peak (0.62 e Å^{-3}) is 0.94 Å from the P atom, and the remaining peaks are ≤0.56 e Å^{-3}. The observed and calculated structure factor amplitudes (Table S-1), hydrogen atom positional parameters (Table S-2), and anisotropic thermal parameters (Table S-3) are available in the supplementary material. The non-hydrogen atom fractional coordinates are listed in Table II.

Table II. Fractional Coordinates and Their Esd's for $UO_2(NO_3)_2[(i\text{-}C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$

atom	x/a	y/b	z/c
U	0.07761 (2)	0.13681 (2)	0.32351 (1)
P(1)	−0.23365 (16)	0.13914 (18)	0.20083 (8)
O(A)	0.1669 (5)	0.0383 (5)	0.2826 (2)
O(B)	−0.0104 (5)	0.2362 (5)	0.3645 (3)
O(1)	−0.1231 (5)	0.0713 (5)	0.2452 (2)
O(2)	−0.3584 (4)	0.1201 (5)	0.2276 (2)
O(3)	−0.2645 (5)	0.1040 (5)	0.1235 (2)
O(4)	0.0324 (5)	0.2653 (5)	0.2233 (2)
O(5)	−0.0387 (5)	−0.0390 (5)	0.3644 (3)
O(6)	0.1452 (5)	0.0103 (5)	0.4313 (3)
O(7)	0.0321 (6)	−0.1388 (6)	0.4598 (3)
O(8)	0.2372 (5)	0.3051 (5)	0.3229 (2)
O(9)	0.2873 (5)	0.1858 (5)	0.4092 (3)
O(10)	0.4178 (6)	0.3359 (7)	0.4002 (3)
N(1)	−0.0536 (6)	0.3704 (5)	0.1273 (3)
N(2)	0.0458 (6)	−0.0585 (6)	0.4203 (3)
N(3)	0.3183 (7)	0.2785 (7)	0.3792 (3)
C(1)	−0.1966 (7)	0.2978 (7)	0.2009 (4)
C(2)	−0.0663 (7)	0.3127 (7)	0.1835 (3)
C(3)	0.0789 (7)	0.3813 (7)	0.1143 (4)
C(4)	0.1118 (9)	0.2746 (10)	0.0738 (5)
C(5)	−0.1621 (7)	0.4282 (7)	0.0771 (3)
C(6)	−0.1779 (9)	0.5606 (7)	0.0929 (4)
C(7)	−0.4911 (7)	0.1615 (7)	0.1910 (4)
C(8)	−0.5389 (11)	0.2443 (11)	0.2393 (6)
C(9)	−0.5706 (10)	0.0483 (10)	0.1721 (8)
C(10)	−0.1903 (12)	0.0124 (11)	0.0928 (6)
C(11)	−0.1935 (16)	0.0576 (15)	0.0219 (8)
C(12)	−0.2392 (16)	−0.1112 (14)	0.0948 (8)
C(10′)	−0.2979 (35)	−0.0026 (32)	0.0891 (17)
C(11′)	−0.3909 (50)	0.0183 (49)	0.0222 (27)
C(12′)	−0.1665 (57)	−0.0500 (57)	0.0865 (29)

Results and Discussion

The combination of diisopropyl (*N*,*N*-diethylcarbamyl)methylenephosphonate (DiPDECMP) and $UO_2(NO_3)_2{\cdot}6H_2O$ in ethanol with a ligand:metal ratio of 2 results in the formation of a light yellow solid, **1**. Elemental analyses indicate that the solid contains only *one* neutral DiPDECMP ligand and two nitrate ions bonded to a UO_2^{2+} group, and this is consistent with eq 1.

$$\text{DiPDECMP} + UO_2(NO_3)_2{\cdot}6H_2O \xrightarrow{\text{EtOH}} UO_2(NO_3)_2(\text{DiPDECMP}) + 6H_2O \quad (1)$$

The infrared spectrum of **1**, recorded from a KBr pellet, displays strong absorptions at 1607 and 1192 cm^{-1}, which can be tentatively assigned to the C=O and P=O stretching

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(9) Several structure refinements of DiPDECMP–metal complexes have been complicated by large thermal motions in the isopropyl groups. Consequently, intensity data for the uranyl complex were collected at a convenient low temperature (−28 °C).

(10) Sheldrick, G. M. "Nicolet SHELXTL Operations Manual"; Nicolet XRD Corp.: Cupertino, CA, 1981. SHELXTL uses scattering factors complied in: "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. IV.

(11) A general description of the least-squares algebra is found in: Ahmed, F. R., Hall, S. R., Huber, C. P., Eds. "Crystallographic Computing"; Munksgaard Publishing Co.: Copenhagen, 1970; p 187.

(12) The weighting scheme used was $w = [\sigma^2(F_0) + gF^2]^{-1}$, where $g = 0.00029$.

frequencies, respectively.[3-6] Both absorptions in **1** appear at significantly lower frequencies than the corresponding frequencies in the free ligand, 1648 and 1253 cm^{-1}, and such down-frequency shifts, $\Delta\nu_{CO} = -41$ cm^{-1} and $\Delta\nu_{PO} = -61$ cm^{-1}, have been used previously to indicate bidentate coordination of C=O and P=O groups with a metal ion.[13-15] Similary, Horwitz and co-workers[8] have reported $\Delta\nu_{CO} = -45$ cm^{-1} and $\Delta\nu_{PO} = -69$ to -71 cm^{-1} for a uranyl nitrate–DHDECMP species, but they have concluded that the smaller $\Delta\nu_{CO}$ is consistent with the formation of a weak ligand carbonyl oxygen atom–UO_2^{2+} association or the presence of an uncoordinated ligand C=O group inductively weakened by a strong P=O $\rightarrow$ U interaction. On the other hand, we have observed similar shifts in $Th(NO_3)_4(DiPDECMP)_2$[4] (**2**) and $Sm(NO_3)_3(DiPDECMP)_2$[6] (**3**) of $\Delta\nu_{CO} = -51$ cm^{-1}, $\Delta\nu_{PO} = -93$ to -70 cm^{-1} and $\Delta\nu_{CO} = -55$ to -31 cm^{-1}, $\Delta\nu_{PO} = -47$ cm^{-1}, respectively.[16] On the basis of these shifts, we tentatively assigned bidentate chelation modes for the CMP ligands in **2** and **3**. Single-crystal X-ray diffraction analyses for $Th(NO_3)_4(DEDECMP)_2$[5] and **3**[6] verified that the CMP ligands are neutral and bonded in a bidentate manner in the solid state. Infrared analysis of $Er(NO_3)_3(DiPDECMP)_2{\cdot}H_2O$ (**4**) showed $\Delta\nu_{CO} = -27$ cm^{-1} and $\Delta\nu_{PO} = -46$ cm^{-1}, and from the above discussion these relatively smaller shifts might be interpreted in favor of either bidentate coordination or monodentate phosphoryl coordination by the CMP ligand.[5] A crystal structure analysis showed that only the phosphoryl oxygen atoms are bonded to the Er atom while the carbonyl oxygen atoms are hydrogen bonded to a molecule of water that is oxygen bonded to Er(III). The hydrogen bonding is consequently responsible for the smaller $\Delta\nu_{CO}$ shift in **4**. These observations clearly indicate that great care must be used in deducing CMP ligand denticity and relative coordinate bond strengths from infrared group frequency shifts. With these points kept in mind, the carbonyl and phosphoryl coordination shifts and the absence of protic solvent in **1** appear to be consistent with the assignment of bidentate CMP ligand coordination to the uranyl ion.

The $^{31}P\{^1H\}$ NMR spectrum for **1** consists of a singlet centered at 25.5 ppm, which is downfield of the resonance for the neat ligand, 22.0 ppm, and the singlets observed for **2**,[5] 22.9 ppm, and **3**,[6] 21.1 ppm. These small downfield shifts are typical of those found in other phosphoryl–metal complexes.[18,19] The $^{13}C\{^1H\}$ spectrum for **1** can be fully assigned, and comparisons of chemical shifts for the methylene carbon atom spanning the C=O and P=O groups and the carbonyl carbon atom with the data for DiPDECMP, **2**, and **3** are of interest.[20] For DiPDECMP, **1**, **2**, and **3**, the methylene resonance is a doublet with δ 34.81, 30.85, 30.46, and 31.57 and $^1J_{PC} = 133.6$, 143.9, 141.2, and 140.4 Hz, and the carbonyl resonance is a doublet with δ 169.2, 171.2, 167.7, and 166.0 and $^2J_{PC} = 5.7$, 5.8, 8.3, and 5.9 Hz, respectively. Therefore, the methylene resonances for the metal complexes are shifted slightly upfield from the free ligand and the $^1J_{PC}$ coupling constants are slightly larger for the complexes than for the free ligand. However, on the basis of this limited set of data, the carbonyl ^{13}C resonances and the phosphoryl ^{31}P resonances show no clear trends that would predict a specific coordination mode.

The analytical and spectroscopic data outlined above are consistent with the formation of the complex $UO_2(NO_3)_2$-(DiPDECMP); however, the denticity of the CMP ligand

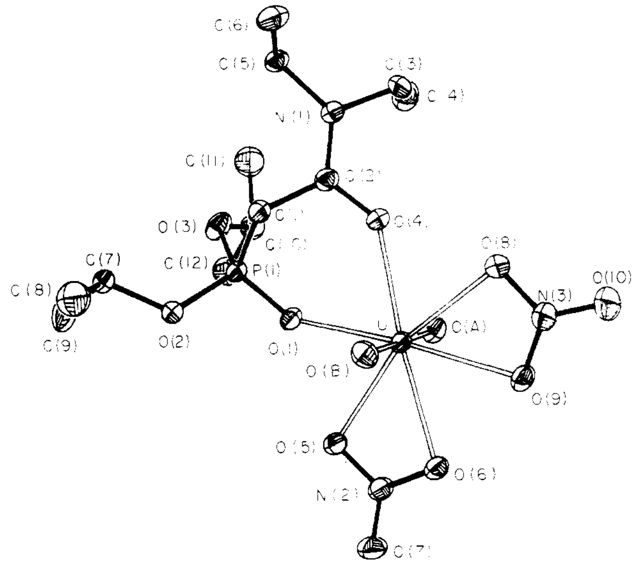

Figure 1. Molecular geometry and labeling scheme in $UO_2(NO_3)_2[(C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$ (25% probability ellipsoids).

Table III. Selected Interatomic Distances (Å)

U–O(A)	1.757 (5)	C(10)–C(11)[a]	1.48 (4)
U–O(B)	1.755 (6)	C(10)–C(12)[a]	1.47 (5)
U–O(1)	2.420 (4)	C(1)–C(2)	1.501 (11)
U–O(4)	2.406 (5)	C(2)–O(4)	1.260 (8)
U–O(5)	2.522 (5)	C(2)–N(1)	1.326 (9)
U–O(6)	2.522 (5)	N(1)–C(3)	1.482 (10)
U–O(8)	2.496 (5)	N(1)–C(5)	1.473 (8)
U–O(9)	2.509 (5)	C(3)–C(4)	1.511 (13)
P(1)–O(1)	1.485 (5)	C(5)–C(6)	1.503 (11)
P(1)–O(2)	1.545 (5)	N(2)–O(5)	1.271 (7)
P(1)–O(3)	1.553 (5)	N(2)–O(6)	1.265 (9)
P(1)–C(1)	1.782 (8)	N(2)–O(7)	1.215 (9)
O(2)–C(7)	1.486 (8)	N(3)–O(8)	1.275 (7)
O(3)–C(10)[a]	1.43 (3)	N(3)–O(9)	1.261 (9)
C(7)–C(8)	1.497 (15)	N(3)–O(10)	1.207 (9)
C(7)–C(9)	1.494 (13)		

[a] Averaged distance for disordered position.

Table IV. Selected Interatomic Bond Angles (deg)

O(A)–U–O(B)	179.5 (2)	O(6)–U–O(8)	111.0 (2)
O(A)–U–O(1)	89.8 (2)	O(5)–U–O(9)	110.9 (2)
O(A)–U–O(4)	89.5 (2)	O(6)–U–O(9)	60.6 (2)
O(A)–U–O(5)	92.1 (2)	U–O(4)–C(2)	137.6 (5)
O(A)–U–O(6)	89.3 (2)	U–O(1)–P(1)	132.6 (3)
O(A)–U–O(8)	91.0 (2)	O(1)–P(1)–O(2)	109.4 (3)
O(A)–U–O(9)	88.3 (2)	O(1)–P(1)–O(3)	114.9 (3)
O(B)–U–O(1)	90.7 (2)	O(2)–P(1)–O(3)	108.7 (3)
O(B)–U–O(4)	90.3 (2)	O(1)–P(1)–C(1)	110.4 (3)
O(B)–U–O(5)	88.4 (2)	O(2)–P(1)–C(1)	109.6 (3)
O(B)–U–O(6)	90.8 (2)	O(3)–P(1)–C(1)	103.7 (3)
O(B)–U–O(8)	88.5 (2)	O(4)–C(2)–C(1)	118.0 (6)
O(B)–U–O(9)	91.3 (2)	N(1)–C(2)–O(4)	119.9 (7)
O(1)–U–O(4)	70.4 (2)	N(1)–C(2)–C(1)	122.1 (6)
O(5)–U–O(6)	50.3 (2)	P(1)–C(1)–C(2)	108.5 (5)
O(8)–U–O(9)	50.4 (2)	O(5)–N(2)–O(6)	115.4 (6)
O(5)–U–O(1)	64.4 (2)	O(5)–N(2)–O(7)	121.9 (6)
O(6)–U–O(1)	114.6 (2)	O(6)–N(2)–O(7)	122.7 (6)
O(5)–U–O(4)	134.7 (2)	O(8)–N(3)–O(9)	114.2 (6)
O(6)–U–O(4)	174.9 (2)	O(8)–N(3)–O(10)	122.0 (7)
O(5)–U–O(8)	160.9 (1)	O(9)–N(3)–O(10)	123.7 (6)

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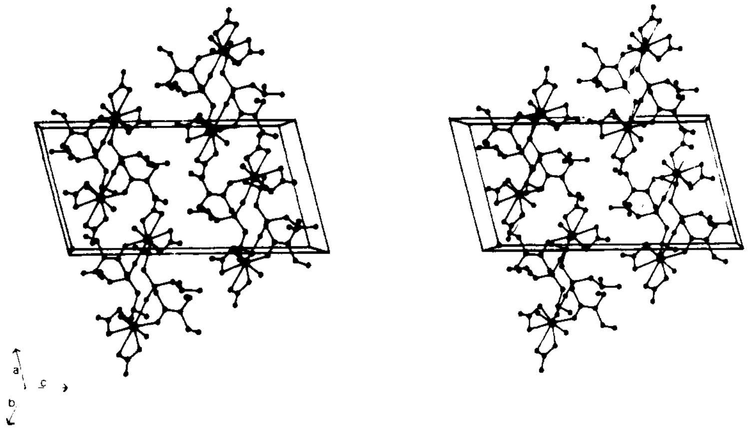

Figure 2. Stereoview of the molecular packing for $UO_2(NO_3)_2[(C_3H_7O)_2P(O)CH_2C(O)N(C_2H_5)_2]$.

cannot be unequivocally established. Consequently, a single-crystal X-ray structure determination of **1** was completed. The X-ray analysis confirms the composition, and the structure is found to contain discrete monomeric units with four molecules per unit cell. A view of the molecular unit is shown in Figure 1, and a stereoview of the crystal packing is shown in Figure 2. Selected interatomic bond distances and angles are summarized in Tables III and IV.

The UO_2^{2+} group is surrounded by an approximately planar[21] belt of six equatorial oxygen atoms provided by two bidentate nitrate ions and a bidentate DiPDECMP ligand. The eight oxygen atom positions form an irregular hexagonal bipyramid, which resembles the coordination polyhedra in $UO_2(NO_3)_2[(C_4H_9)_3PO]_2$[22] (**5**), $UO_2(NO_3)_2[(C_6H_5)_3AsO]_2$[23] (**6**), $UO_2(NO_3)_2(H_2O)_2$[24] (**7**), and $UO_2(NO_3)_2(C_3H_7O_2N)_2$[25] (**8**). The uranyl U–O distances in **1**, U–O(A) = 1.757 (5) Å and U–O(B) = 1.755 (6) Å, are similar to those found in **5**, 1.742 (7) Å, **6**, 1.71 (3) Å, **7**, 1.763 (5) and 1.754 (4) Å, and **8**, 1.73(2) Å. As expected, the O(A)–U–O(B) unit is essentially linear, 179.5 (2)°. The uranium–phosphoryl oxygen atom bond distance in **1** is 2.420 (4) Å, which is slightly longer than the corresponding distance in **5**, 2.347 (6) Å, and in the seven-coordinate complex $UO_2(NCS)_2[(C_6H_5)_3PO]_2[(CH_3)_2CO]$ (**9**), 2.37 (2) Å (av).[26] The uranium–carbonyl oxygen atom bond distance in **1** is 2.406 (5) Å, which is similar to the related distances in the ethylcarbamate complex **8**, 2.40 (2) Å, and in $UO_2[(CF_3CO)_2CH]_2{\cdot}THF$[27] (**10**), 2.38 (2) Å (av), and significantly shorter than the uranium–acetonyl oxygen atom bond distance in **9**, 2.56 (2) Å. The average uranium–nitrate oxygen atom distance in **1**, 2.512 (5) Å, is similar to the related distances in several uranyl nitrate complexes: **5**, 2.530 (8) and 2.535 (8) Å; **6**, 2.58 (4) Å; **7**, 2.497 (5) Å; **8**, 2.53 (2) Å. The in-plane O–U–O angles range from 70.4 (2)° for the DiPDECMP "bite" angle to 50.4 (2) and 50.3 (2)° for the nitrate "bite" angles, and these compare with the ideal angle of 60° for a regular hexagon.

The structural parameters for the coordinated DiPDECMP ligand in **1** are similar to those found in other CMP–metal complexes.[3,5,6] The phosphoryl bond distance, P(1)–O(1) = 1.485 (5) Å, is similar to the P=O bond distances in the bidentate CMP ligand complexes **2**, 1.478 (4) Å, and **3**, 1.480 (2) Å, and longer than the distance in the monodentate erbium complex **4**, 1.466 (7) Å. The P=O distances in the monodentate phosphoryl complexes **5** and **9** are 1.489 (7) Å and 1.47 (2) and 1.48 (2) Å, respectively. The carbonyl distance C(2)–O(4) = 1.260 (8) Å is in agreement with the metal-coordinated carbonyl distances in **2**, 1.256 (6) Å, **3**, 1.261 (3) Å, **9**, 1.27 (3) Å, and **10**, 1.30 (3) Å. The bond angles within the ligand backbone are very similar to those angles found in **2** and **3**.

The planar, bidentate geometry of the nitrate ions in **1** is very similar to the geometries in **2**–**5**. The N–O bond distances, which include the uranyl-bonded oxygen atoms, range from 1.261 (9) to 1.275 (7) Å, and these distances are longer than the N–O distances containing the unbound oxygen atoms: N(2)–O(7) = 1.215 (9) Å and N(3)–O(10) = 1.207 (9) Å. The O–N–O angles between the uranyl-bonded oxygen atoms, 115.4 (6) and 114.2 (6)°, are reduced from the ideal 120° as expected, while the remaining O–N–O angles are greater than 120°.

The major difference between the molecular structure of **1** and the structures of many other eight-coordinate uranyl nitrate–ligand complexes is the formation in **1** of a stable six-membered chelate ring with cis orientation of the P=O and C=O groups. Normally in $UO_2(NO_3)_2L_2$ complexes monodentate ligands are trans to each other. In those complexes containing potentially bidentate ligands, trans monodentate bis(ligand) structures have been proposed. For example, Lestas and Truter[28] reported the isolation of a single complex from the combination of $UO_2(NO_3)_2{\cdot}6H_2O$ and variable amounts of the potentially bidentate ligand $Ph_2P(O)CH_2C(O)Ph$. On the basis of elemental analyses and infrared spectra, it was concluded that the resulting complex contained two trans monodentate ligands with U—O=P interactions. Unfortunately, a confirming X-ray diffraction structural analysis of this compound has not appeared. Apparently the only other examples of bidentate $UO_2(NO_3)_2L$ complexes are provided by a series of diphosphonates, $UO_2(NO_3)_2[R_2P(O)CH_2P(O)R_2]$, reported by Siddall and Prohaska.[29] The monoligate stoichiometry was deduced from elemental analyses, and the bidentate phosphonate coordination in $CDCl_3$ solutions was proposed on the basis of ^1H NMR data.

The crystal structure determination for **1** reported here provides unequivocal evidence for cis, bidentate coordination of the uranyl ion by a single carbamylmethylenephosphonate

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(21) A planes calculation (supplementary material, Table S-4) shows the following atomic deviations (Å) from the equatorial plane: U, –0.0012; O(1), –0.0383; O(4), –0.0197; O(5), 0.0688; O(6), –0.0294; O(8), 0.0692; O(9), 0.0494.

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ligand. In addition, this structure and the structures for related thorium and samarium complexes indicate a strong tendency in the solid state for the CMP ligands to act as bidentate chelating ligands where steric factors permit.

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Supplementary Material Available: Listings of structure factors, hydrogen atom positional parameters, thermal parameters, and a least-squares plane (16 pages). Ordering information is given on any current masthead page.

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Crystal Structure Determination of Bis(tetraphenylphosphonium) Heptasulfide, $(Ph_4P)_2S_7$

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The S_7^{2-} anion has been obtained by the reaction of MoS_9^{2-} with an excess of the sodium salt of the diethyldithiocarbamate anion in acetonitrile solution. The tetraphenylphosphonium salt of S_7^{2-}, $(Ph_4P)_2S_7$ (I), crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ and lattice parameters $a = 11.041$ (3) Å, $b = 18.589$ (4) Å, $c = 12.040$ (3) Å, $\alpha = 74.58$ (3)°, $\beta = 69.05$ (3)°, $\gamma = 87.76$ (4)°, and $V = 2220.18$ Å^3. Diffraction data (Mo Kα radiation, $2\theta_{max} = 50°$) were collected with a Picker FACS-I automated diffractometer, and the structure was solved and refined by direct methods and full-matrix least-squares procedures to $R_F = 5.8\%$ and $R_{wF} = 8.7\%$ with use of 5102 unique reflections. The S_7^{2-} ion is found to be a right-handed nonbranched S(1)S(2)S(3)S(4)S(5)S(6)S(7) helix with very short terminal sulfur–sulfur bonds of 1.990 (2) and 1.995 (2) Å for S(1)–S(2) and S(6)–S(7), respectively. The internal bond distances are as follows (in Å): S(2)–S(3), 2.036 (2); S(3)–S(4), 2.062 (2); S(4)–S(5), 2.062 (2); S(5)–S(6), 2.037 (2). The torsion angles in the chain are as follows (in degrees): S(2)–S(3), 73.28 (10)°; S(3)–S(4), 74.41 (10)°; S(4)–S(5), 65.22 (10)°; S(5)–S(6), 79.86 (10)°. The $(Ph_4P)_2S_7$ salt dissolves in polar solvents to give blue solutions with adsorption bands at 610, 470, 345 (sh), and 304 nm.

Introduction

Various polysulfide anions have been characterized structurally to date in salts such as K_2S_2,[1] Na_2S_2,[1], BaS_3,[2] $BaS_4{\cdot}H_2O$,[3] Na_2S_4,[4] K_2S_5,[5] Tl_2S_5,[6] and Cs_2S_6.[7] The S_x^{2-} anions (x = 4–6) in these salts are doubly charged, nonbranched nonlinear sulfur chains. The preparation, certain properties, and lattice constants of the $C_3H_{12}N_2^{2+}S_7^{2-}$ salt have been reported[8] about 25 years ago; however, no other recent structural study of a heptasulfide or higher order polysulfide is available. In a attempt to replace the S_4^{2-} chelating ligands in the MoS_9^{2-} complex[9] by diethyldithiocarbamate ligands (in the presence of Ph_4PCl), we isolated an orange-red crystalline material, which was identified by elemental analysis as $(Ph_4P)_2S_7$. In this paper we report on the crystal and molecular structure of $(Ph_4P)_2S_7$, which contains the S_7^{2-} anion.

Experimental Section

Preparation of $(Ph_4P)_2S_7$. A 0.5- (0.9-mmol) of quantity of $(Et_4N)_2MoS_9$ and 0.6k g (1.8 mmol) of Ph_4PCl were added to ca. 50 mL of CH_3CN. To this heterogeneous solution was added 1.1 g (4.9 mmol) of sodium diethyldithiocarbamate trihydrate, and the mixture was heated for 15 min. The resulting deep green solution changed to brown after cooling to ambient temperature. Upon addition of ether, following filtration, crystalline unreacted $(Et_4N)_2MoS_9$ was deposited and removed by a subsequent filtration. The volume of the filtrate was reduced to dryness in vacuo, leaving an oily brown residue, which was then washed with two 10-mL portions of diethyl ether. The brown oil was dissolved in a minimum amount of CH_3CN (~30 mL), resulting in a blue solution to which diethyl ether was added (~20 mL) to initiate crystallization. When the solution stood for ca. 2 h, 0.15 g of analytically pure orange-red crystals was deposited and

Table I. Summary of Crystallographic Data and Data Collection Procedures

formula	$Ph_8P_2S_7$
fw	902
space group	$P\bar{1}$
a, Å	11.041 (3)
b, Å	18.589 (6)
c, Å	12.040 (3)
α, deg	74.58 (3)
β, deg	69.05 (3)
γ, deg	87.76 (4)
V, Å^3	2220.18
d_{calcd}, g/cm^3	1.35
d_{obsd},[a] g/cm^3	1.35
Z	2
cryst size, mm	0.16 × 0.21 × 0.52
μ(Mo Kα), cm^{-1}	4.49
radiation	graphite monochromatized Mo Kα ($\lambda_{\bar{\alpha}} = 0.710\,73$ Å)
scan type	θ–2θ
step size	0.12–0.16
no. of steps	7–15
max counting time, s	4
time/step, s	4
data collection range, deg	$3 < 2\theta < 50$
bkgd time, s	8
no. of unique data	5102
no. of data, $F_o^2 > 3\sigma(F_o^2)$	7251
p[b]	0.06
cryst decay	negligible
no. of variables	514
R	0.058
R_w	0.087

[a] By flotation in a CCl_4/pentane mixture. [b] "Ignorance" factor, $\sigma^2(F^2) = (0.06F^2) + \sigma^2(F^2)$ (from counting statistics).

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